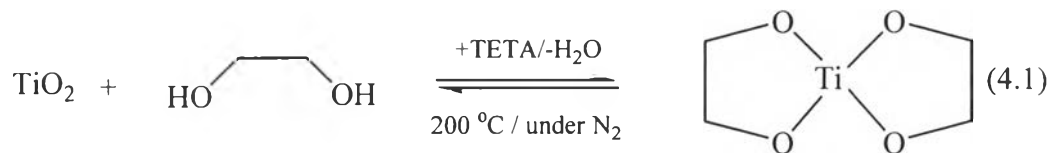# CHAPTER IV
RESULTS AND DISSCUSSION

4.1 Synthesis of Glycolato Titanium Precursor

Glycolato titanium precursor was synthesized via the "Oxide One Pot Synthesis" (OOPS) process using inexpensive and widely available TiO_2 as starting material, ethylene glycol and triethylenetetramine, TETA, as a base (Phonthammachai et al., 2003). Since water is a by-product of the reaction, it must be removed from the system to push the reaction forward, as illustrated in equation 4.1.

$$TiO_2 + HO\diagup\diagdown OH \underset{200\ ^\circ C\ /\ under\ N_2}{\overset{+TETA/-H_2O}{\rightleftharpoons}} \left[\begin{array}{c} O \diagup \diagdown O \\ Ti \\ O \diagdown \diagup O \end{array}\right] \quad (4.1)$$

4.1.1 Characterization of Titanium Glycolate Precursor

The synthesized and purified precursor was identified using TGA, FAB$^+$-MS, and FT-IR, as described following

4.1.1.1 *Thermal gravimetric analysis (TGA)*

The TGA analyses of glycolato titanium were carried out in nitrogen atmosphere and the result is shown in figure 4.1. The first weight loss around 310°-350°C corresponds to organic ligand decomposition of remaining organic residue. The final ceramic yield is 46.95%, as compared to 47.56% for the theoretical ceramic yield based on a final ceramic product of TiO_2.
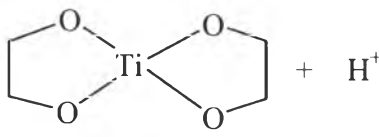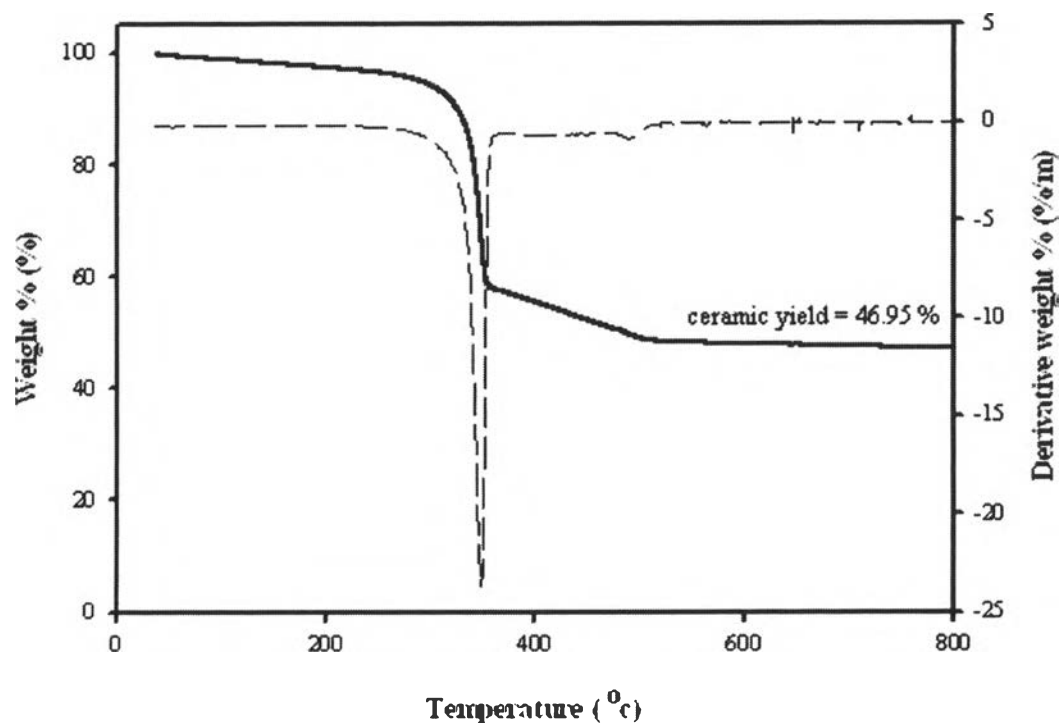
Figure 4.1 TGA profile of glycolato titanium.

4.1.1.2 *FAB⁺-mass spectroscopy (FAB⁺-MS)*

Mass spectral analysis of glycolato titanium shows the peak at m/e 169, 8.5 % intensity, indicating the molecular ion of glycolato titanium which is easily broken to the peak at m/e 93 that is belong to ethoxy titanium. The fragment peaks at m/e 45 and 28 correspond to the ethoxy group and ethylene, respectively. The intensities of all proposed structures are shown in table 4.1

Table 4.1 The proposed structure and the pattern of fragmentation of glycolato
titanium

m/e	% Intensity	Proposed Structure
169	8.5	$+ \ H^+$
93	100	$Ti\text{-}OCH_2CH_2 \quad + \ H^+$
45	13	$CH_2CH_2O \quad + \ H^+$
28	4	$CH_2CH_2{}^\bullet$

4.1.1.3 *Fourier transform infrared spectroscopy (FTIR)*

IR spectrum and assignment of glycolato titanium are shown in Figure 4.2 and Table 4.2, respectively. The band around 2855-2927 cm^{-1} is assigned to the C-H stretching of glycolate ligand. Three bands at 1130, 1080 and 1042 cm^{-1} can be assigned to C-O-Ti, characteristics of glycolate ligand linked to titanium. The presence of the band at 619 cm^{-1} is assigned to Ti-O stretching (Wang *et al.*, 1999).
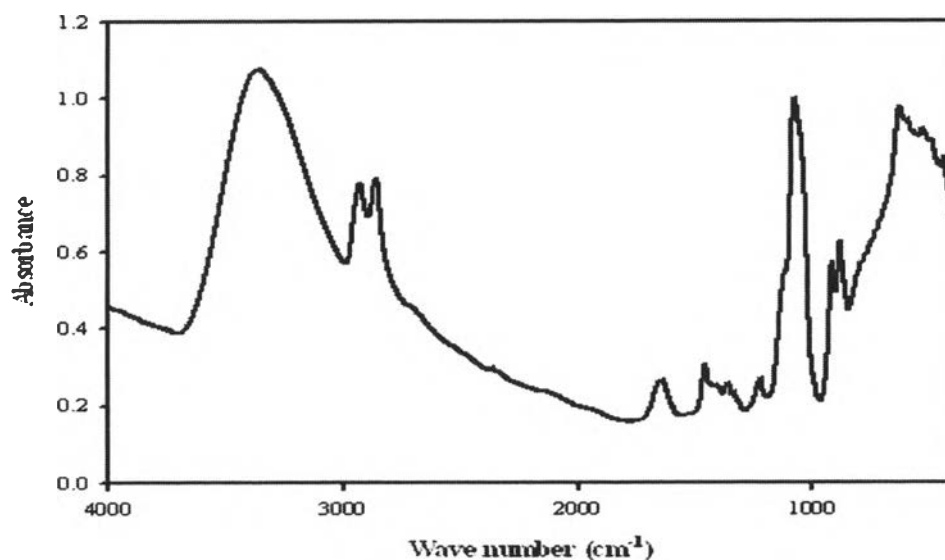
Figure 4.2 IR spectrum of glycolato titanium.

Table 4.2 Assignment of IR spectrum of glycolato titanium

Peak Positions (cm-1)	Assignments
3000-3500	O-H stretching (from ethylene glycol)
2855-2927	C-H stretching
1430-1450	C-H bending
1040-1130	C-O-Ti
610-650	Ti-O stretching

4.2 Synthesis of Silatrane Precursor

Silatrane (tris(silatranyloxy-ethyl)amine or SiTEA) was synthesized following Wongkasemjit's method (Piboonchaisit *et al.*, 1999) by reacting Triethanolamine with silicon dioxide using ethylene glycol as solvent at 200°C under nitrogen atmosphere.

4.2.1 <u>Characterization of Silatrane Precursor</u>

The synthesized and purified precursor was identified using TGA, FAB$^+$-MS, and FT-IR, as described following.

4.2.1.1 *Fourier transform infrared spectroscopy (FT-IR)*

Assignment of IR spectrum of silatrane is shown in table 4.3. The band around 2800-3000 cm^{-1} is assigned to the C-H stretching of ligand. The presence of band at 1040-1180 cm^{-1} is assigned to Si-O stretching. Two bands at 735, 786 cm^{-1} can be assigned to Si-O-C, characteristics of ligand linked to silicon.

Table 4.3 IR spectrum of silatrane

Peak Positions (cm^{-1})	Assignments
3100-3700	b, ν O-H
2800-3000	s, ν C-H
2750-2670	w, NR$_3$ salt (Si ← N)
1445, 1459, 1493	m, δ C-H
1351	w, ν C-N
1276	m, δ C-O
1040-1180	b & vs, ν Si-O
786	vs, δ Si-O-C
735	s, δ Si-O-C
576	w, Si ← N

4.2.1.2 *Thermal gravimetric analysis (TGA)*

TGA thermogram provides only one mass loss transition at 390°C with 18.5% ceramic yield corresponding to $Si((OCH_2CH_2)_3N)_2H_2$, whose theoretical ceramic yield is 18.6%.
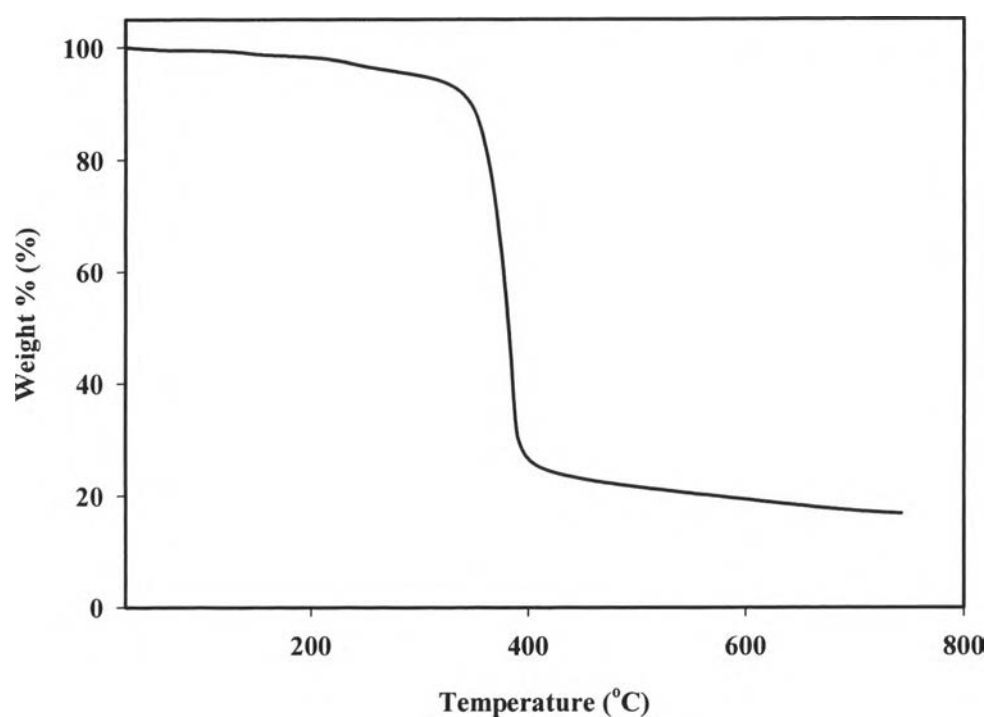
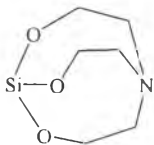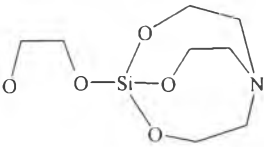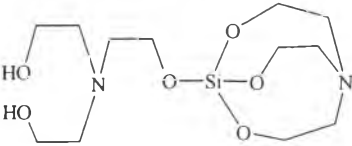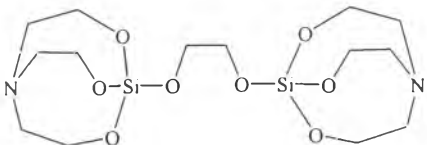**Figure 4.3** TGA profile of silatrane.

4.2.1.3 *FAB^+-mass spectroscopy (FAB^+-MS)*

This technique gives the molecular as well as base peaks at m/e 323 of $Si((OCH_2CH_2)_3N)_2H^+_3$ and m/e = 174 of $Si((OCH_2CH_2)_3N)$, respectively. The intensities of all proposed structures are shown in table 4.4

Table 4.4 The proposed structure and the pattern of fragmentation of silatrane

| m/e	intensity	proposed structure
174	100	
236	11.3	
323	2.6	
409	0.04	

4.3 Synthesis of TS-1 Zeolite

Due to the use of our titanium glycolate and silatrane precursors, it was necessary to study all formulation parameters and reaction conditions that might affect the formation of TS-1.

4.3.1 Effect of Aging and Reaction Times

From the experimental study, to obtain small and fully-grown crystals, the aging time and microwave temperature must reach at 110 hr and 150°C, respectively. After 5 hr of heating, a lot of big crystals of 3.2x1 micron in orthorhombic shape were present, as shown in figure 4.4 (a). The smaller

crystals occur as increasing the reaction heating time from 10 to 15 to 20 hr. The reason is the longer time for nucleation to occur, resulting in smaller crystals. However, the crystals after 20 hr of heating stop growing owing to their complete nucleation.
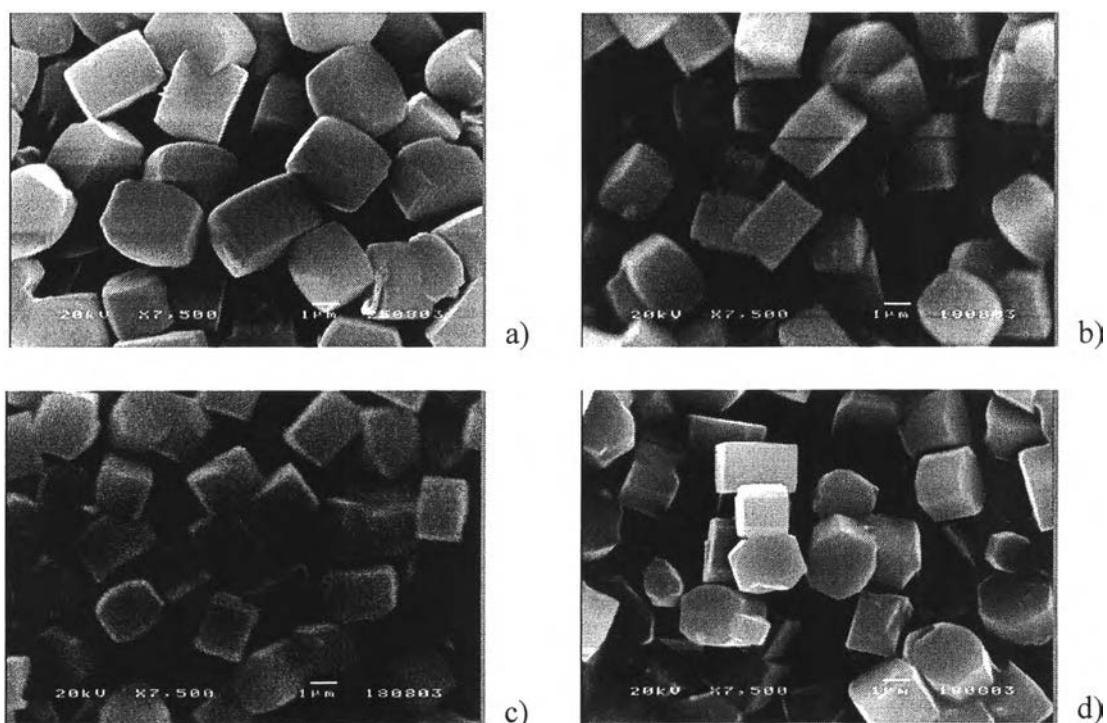

Figure 4.4 Effect of reaction time on TS-1 morphology after 110 hr aging time at 150°C for reaction heating time of: a) 5; b) 10; c) 15 and d) 20 hr.

As mentioned previously, 110 hr aging time is required to produce perfect, very small and fully-grown crystals. This result is illustrated in figure 4.5 (e): when the mixture is aged for longer time, more nucleation of crystal was obtained. Thus, the crystal size was decreased from the aging time of 20-110 hr, as shown in figure 4.5 (a-e). However, too long aging time created bigger crystals. Thus, the crystal size becomes larger when increasing aging time from 110 to 170 hr, as shown in figure 4.5 (e-h). The XRD pattern of TS-1 is shown in figure 4.6.
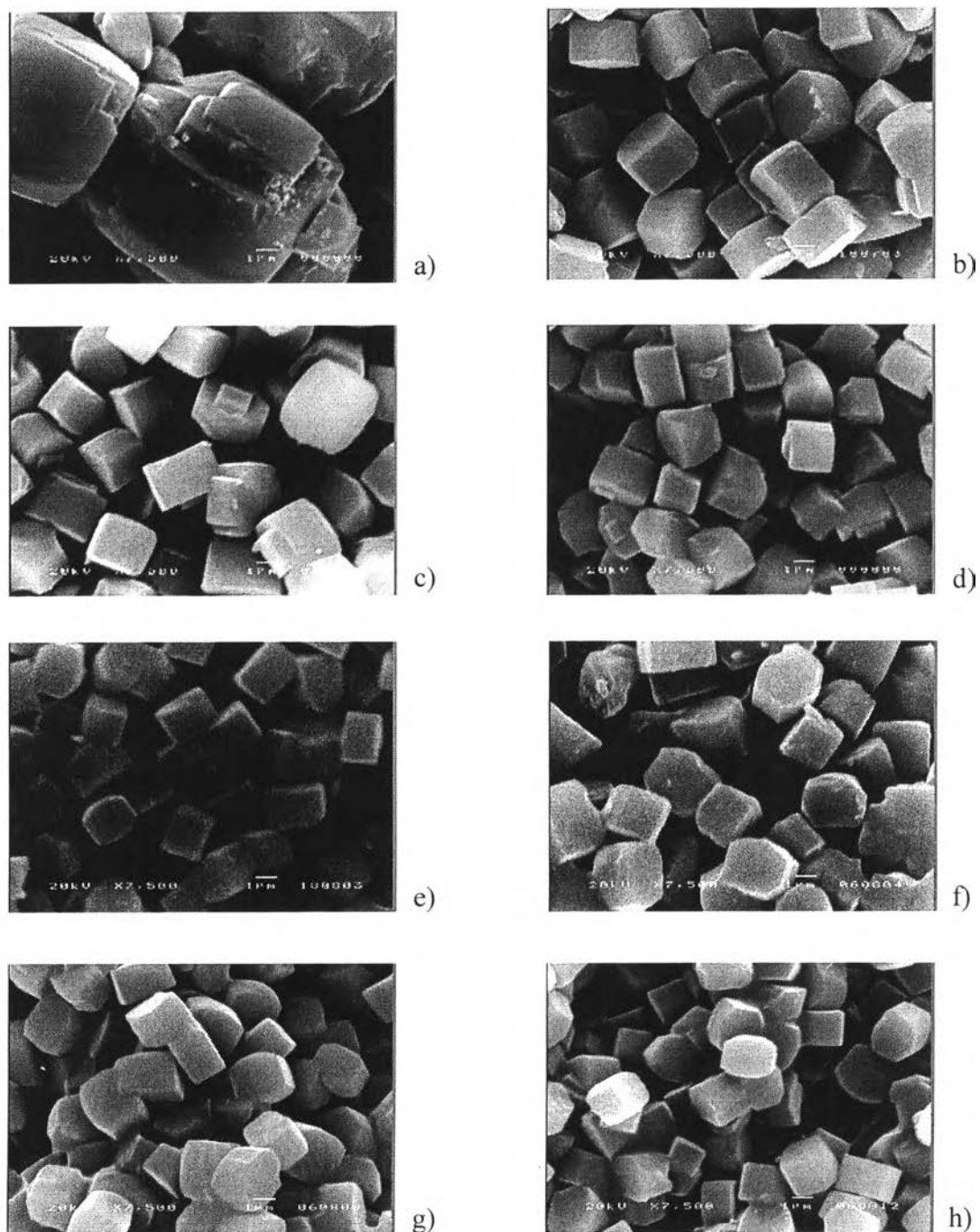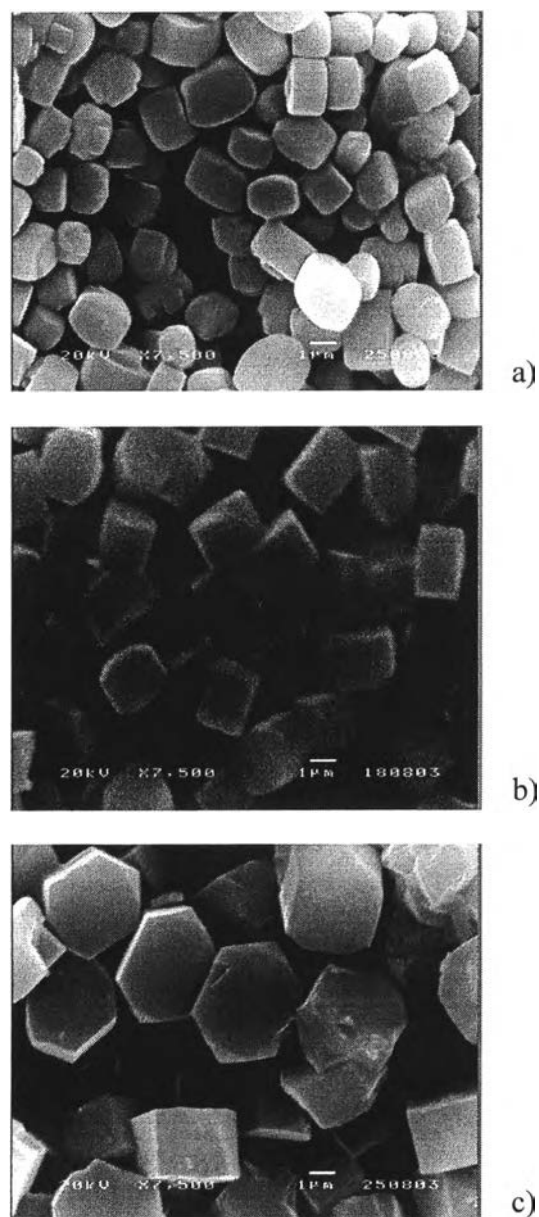
Figure 4.5 Effect of aging time on morphology of products formed after heating
for 15 hr at 150°C: a) 20; b) 60; c) 70; d) 90; e) 110; f) 130; g) 150 and
h) 170 hr.
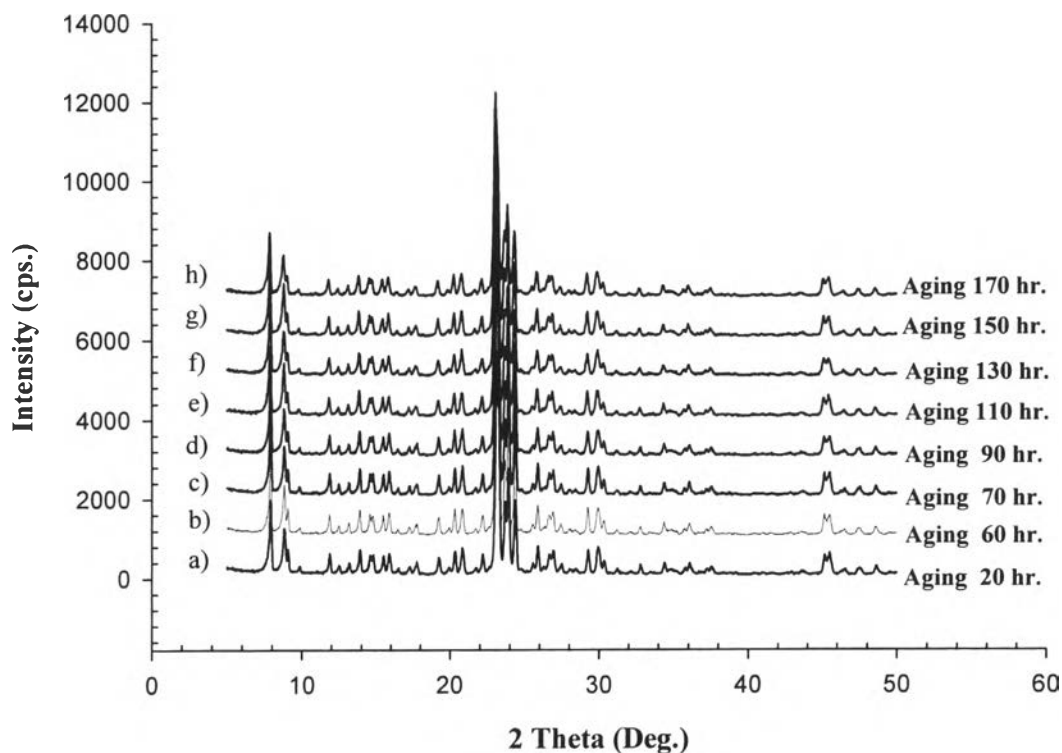
Figure 4.6 Effect of aging time on X-ray diffractograms of products formed after heating for 15 hr at 150°C: a) 20; b) 60; c) 70; d) 90; e) 110; f) 130; g) 150 and h) 170 hr.

4.3.2 Effect of Temperature

It is well known that temperature strongly influences the formation of zeolites, using either organosilicate or inorganic precursors. The optimal temperature range depends on the Si/Ti ratio. We studied the effect of temperature at 120°, 150° and 180°C using the sample ratio of $SiO_2:0.01TiO_2:0.1TPA:0.4NaOH:114H_2O$, for the 110 hr aging time and 15 hr reaction time. SEM results are shown in figure 4.7. Heating at 120°C for 15 hr produces a crystal which is not uniform. But at 150°C, the crystal is more uniform, complete and beautiful. However, at 180°C, the crystal grows in b-direction, resulting in a bigger size and less surface area.

Figure 4.7 Effect of reaction temperature on product morphology formed after 110 hr aging time for the reaction time of: a)120°; b) 150° and c) 180°C.

It appears that MFI formation can be attained using a shorter reaction time and/or aging time with higher temperature. However, use of the microwave technique in zeolite synthesis at high temperature, especially at 180°C, can

degrade the organic template via the Hoffman reaction, as reported by Arafat *et al.* (1992).

4.3.3 Effect of Hydroxide Ion

Hydrolysis of both inorganic and organic precursors occurs in the initial stage of the reaction, and strongly depends on the NaOH/Si ratio. Thus, the role of hydroxide ion in zeolite synthesis is a major factor to be considered. We fixed the formulation at $SiO_2:0.01TiO_2:0.1TPA:xNaOH:$ $114H_2O$ (x = 0.1, 0.3, 0.4, 0.5, 0.7 and 1.0) with reaction conditions of 110 and 15 hr aging and reaction time, respectively, 150°C reaction temperature. SEM results are shown in figure 4.8. At the 0.1 NaOH/Si ratio, no TS-1 is formed. However, as shown in Fig.4.8, crystals are observed from mixtures containing 0.3 to 0.7 NaOH/Si ratio. The crystal size decreases with increasing NaOH/Si ratio.

At the 0.1 NaOH/Si ratio, a white cloudy gel was obtained after 110 hr aging time. Only this condition formed a gel. The formation of gel becomes unfavorable during the aging period due to fast hydrolysis followed by condensation reaction, causing fewer interactions between precursor and TPA. Moreover, lower NaOH also causes fewer nucleation events, as can be seen by the larger crystal size and the presence of amorphous material in the SEM micrographs (figure 4.8(a)).This was confirmed by XRD analysis, which showed a broad amorphous peak (figure 4.9). The broad amorphous XRD peak largely disappears when the NaOH has been increased. At the 0.5 NaOH/Si ratio, the crystal size is bigger and not uniform. Moreover, some secondary growth of crystal also occurs. At the 0.7 NaOH/Si ratio, crystals occur secondary growth and are bigger in size. The higher basic condition causes a higher hydrolysis. Thus, when mixture is condensed, it gives bigger crystal size and secondary growth occurrence of crystal. As shown in figures 4.8 (d-e). At the 1.0 NaOH/Si ratio, crystal fracture appears to occur, as shown in figure 4.8 (f). Possibly, dissolution of crystalline material under highly basic conditions may take place under microwave conditions, as indicated in the

work of Arafat *et al.* (1992). The NaOH/Si ratio of 0.4 appears to be the optimum condition since no amorphous is observed (Fig.4.8 c).
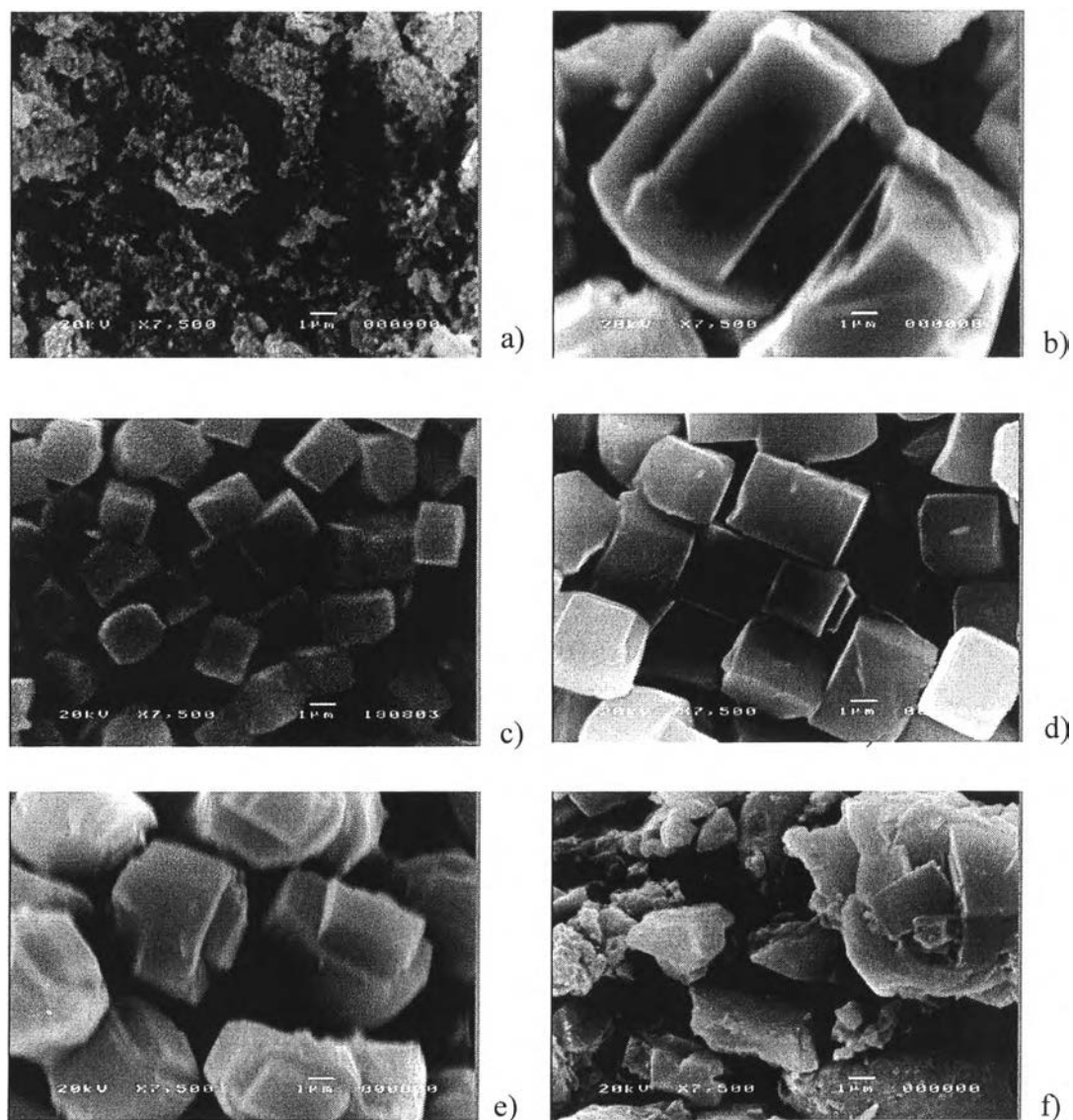
Figure 4.8 Effect of hydroxide concentration on products formed after aging for 110 hr and reaction temperature and time of 150°C and 15 hr, respectively, using NaOH ratio, x, of: a) 0.1; b) 0.3; c) 0.4; d) 0.5; e) 0.7 and f) 1.0.

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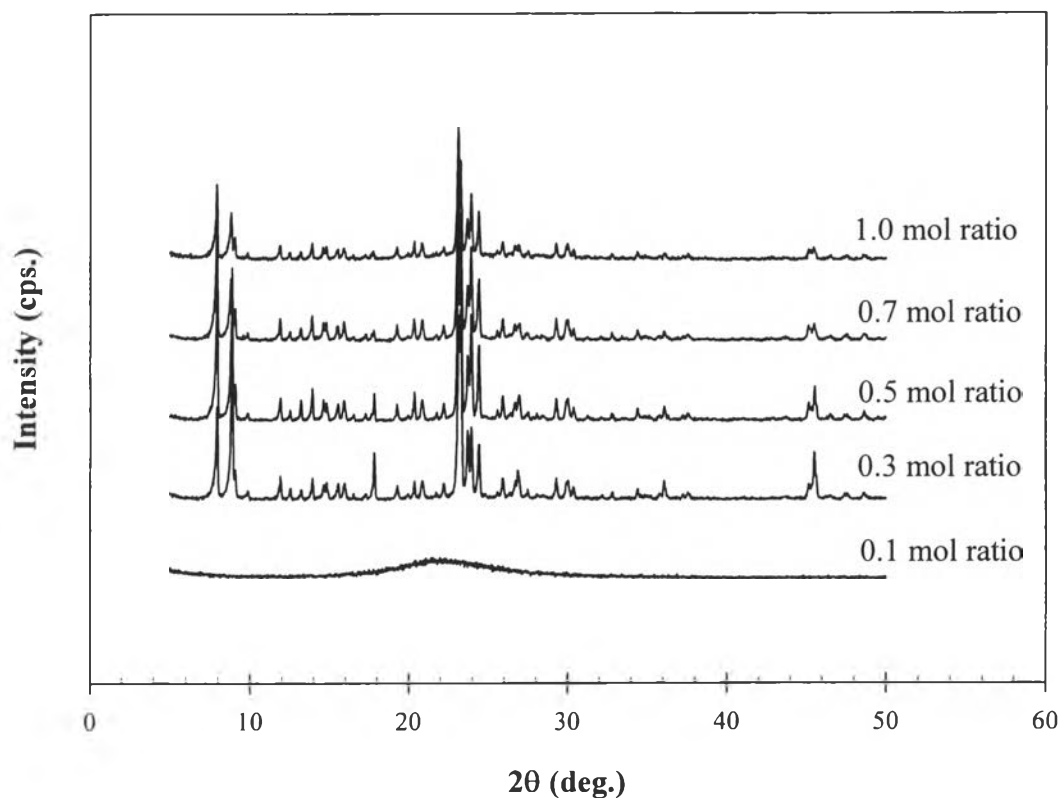
Figure 4.9 XRD patterns of products formed from reaction of
SiO$_2$:0.01TiO$_2$:0.1TPA:xNaOH:114 H$_2$O (x = 0.1, 0.3, 0.5,
0.7 and 1.0) with reaction conditions of 110 and 15 hr aging and
reaction time, respectively, 150°C reaction temperature.

4.3.4 Effect of Template

We studied the effect of template concentration by fixing the
formula at SiO$_2$:0.01TiO$_2$:xTPA:0.4NaOH:114H$_2$O (x = 0.05, 0.1, 0.2, 0.3,
0.4, and 0.5), and reaction conditions at 15 hr heating time, 150°C heating
temperature and 110 hr aging time. As shown in the figure 4.10, the crystal
size at the TPA/Si of 0.05 is the biggest. However, at low TPA concentration
more agglomerate of amorphous silicate is formed. This result is consistent
with our observation of aging time effect that enhances the crystallization rate.

The concentration of template molecule is directly proportional to that of the primary units formed, relating in turn to the number of nucleation sites.

Theoretically, complete conversion should be obtained at the stiochiometric equivalent ratio of the 0.1 TPA/Si ratio. However, our results indicate that some template may not participate in the formation of MFI, possibly due to an interaction between template and partially hydrolyzed organic ligand of silatrane. As a result, MFI has to be synthesized at much higher template concentration. When TPA/Si = 0.2, there is no agglomeration, and the crystal size becomes smaller. Evidently, higher template concentration results in more nucleation events, resulting in smaller crystals. Thus, the crystal size strongly depends on the concentration of organic template, as shown in figure 4.10 (a-f).
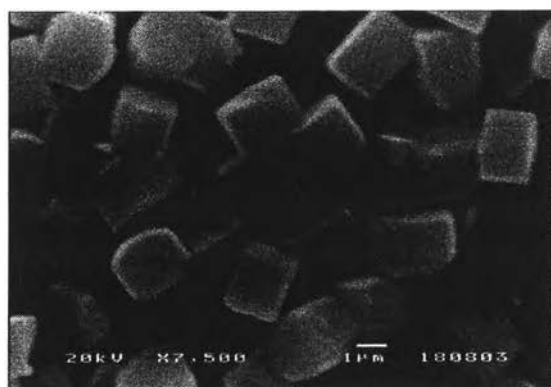
4.3.5 Effect of Dilution

In this study, we conducted reaction using the same sample volume, but different water content. This avoids extraneous factors, which might occur, such as, the pressure created during heating. The reaction formula was SiO_2: $0.01TiO_2$:$0.1TPA$:$0.4NaOH$:xH_2O (x = 114, 140 and 170), and the reaction conditions at110 hr aging time, 150°C reaction temperature for 15 hr. The SEM results are shown in the figure 4.11 Smaller and more complete crystals were synthesized at the H_2O/Si ratio of 114 and elongated crystals were obtained at more dilute condition (H_2O/Si = 140, 170). However, it is worth noted that at very high dilution, the biggest crystal was obtained due to a decrease in nucleation rate from fewer collisions between primary units. Therefore, more concentrated conditions give smaller crystal sizes due to a higher nucleation rate. The observation from SEM that the crystals grow into bigger shapes on dilution is shown in figure 4.11 (a-c).
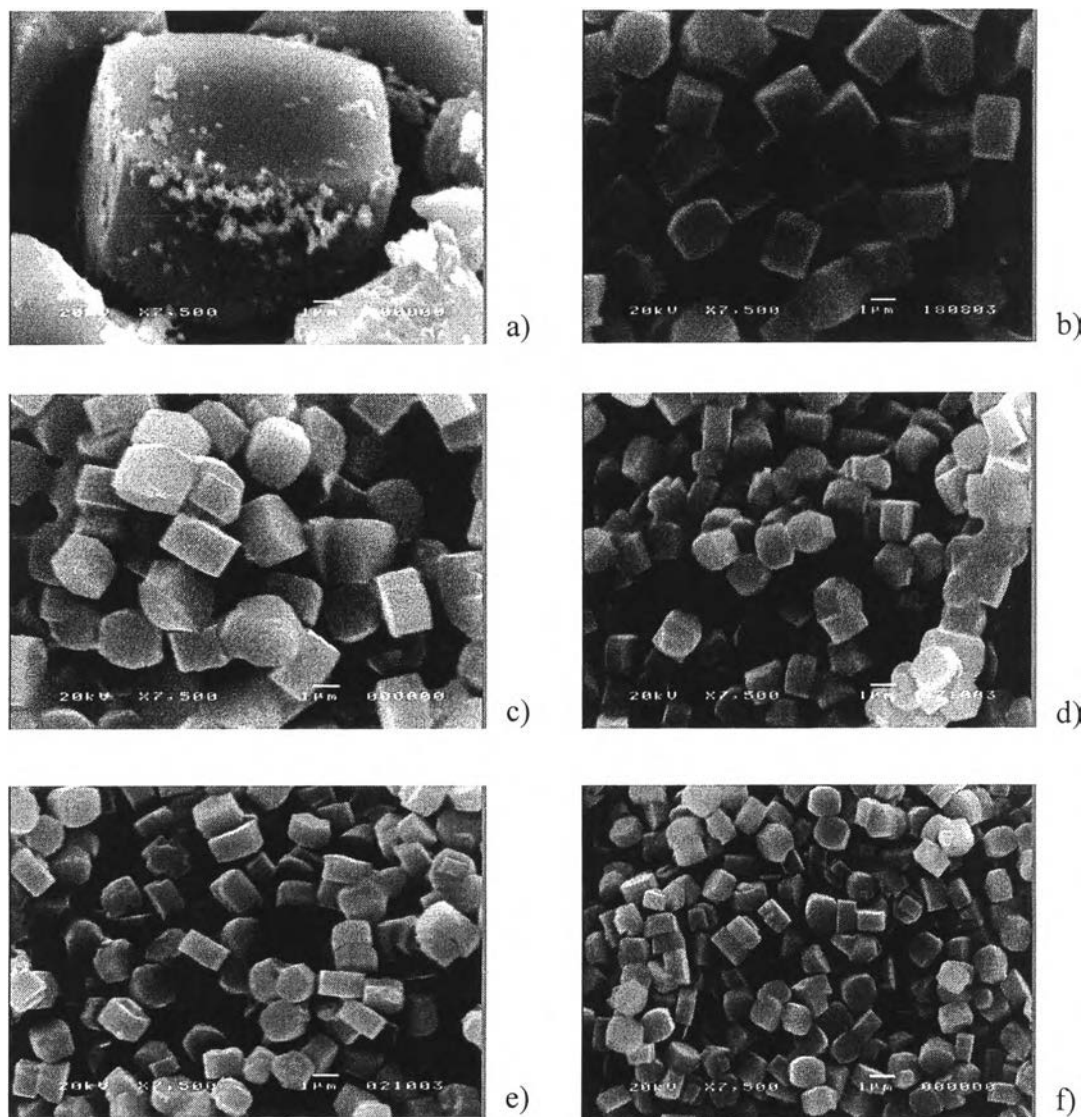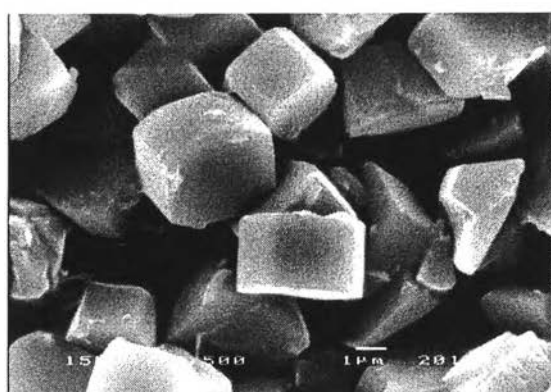
Figure 4.10 Effect of TPA concentration on products formed from SiO_2: $0.01TiO_2$: 0.1 TPA: $0.4NaOH$: $114H_2O$ after aging for 110 hr and reaction temperature at 150°C for 15 hr. TPA/Si ratios, x, are: a) 0.05; b) 0.1; c) 0.2; d) 0.3; e) 0.4 and f) 0.5 mol ratio.
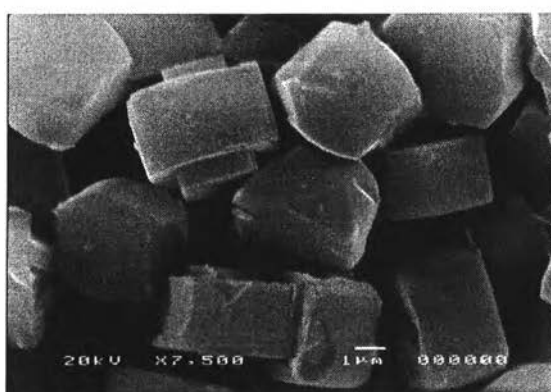
Figure 4.11 Effect of dilution on product morphology formed after aging for 110 hr and heating at 150°C for 15 hr at the water ratio, x, of: a) 114; b) 140; c) 170 mol ratio.
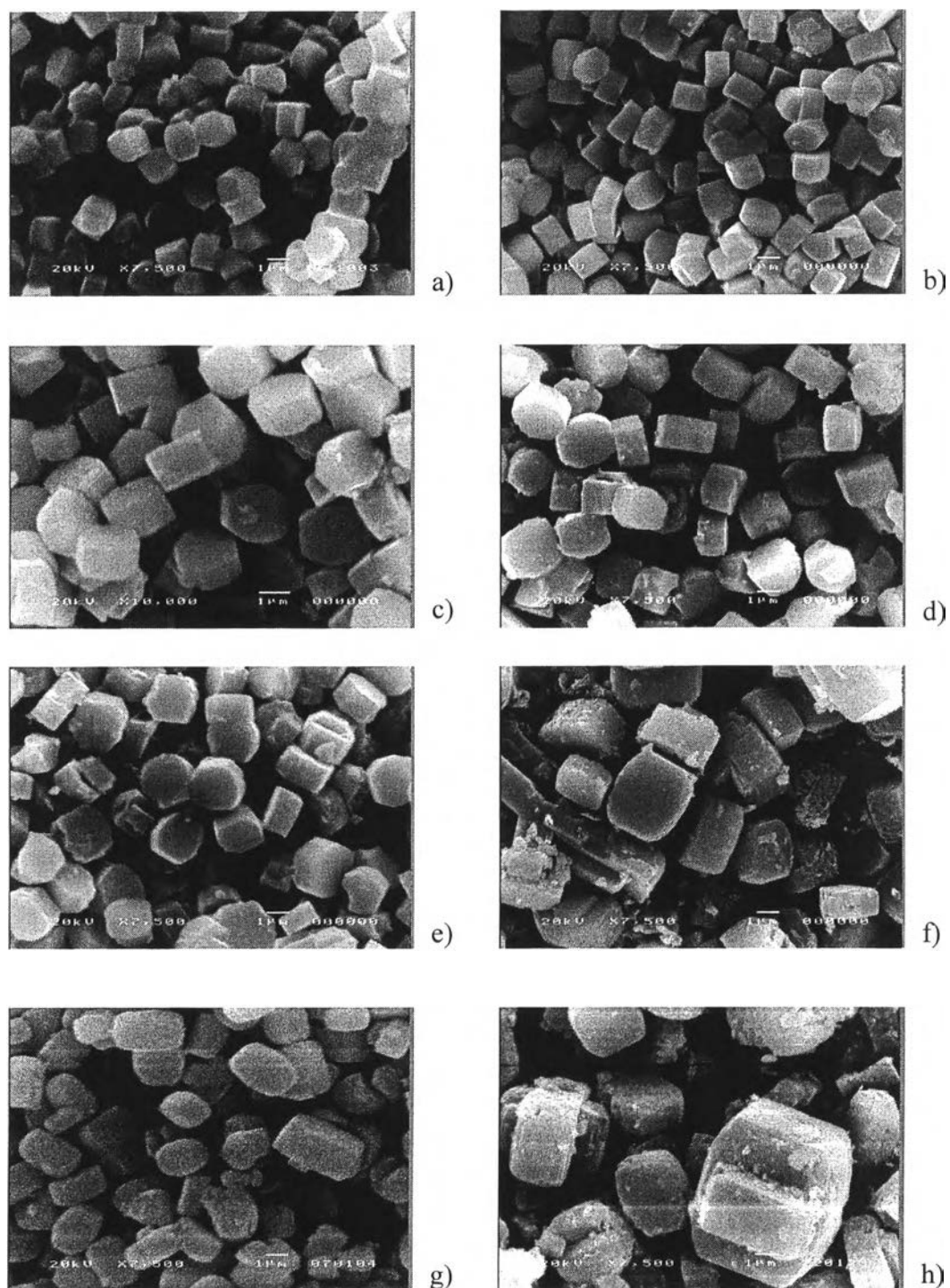
4.3.6 Effect of Si/Ti Ratio

The effect of the Si/Ti ratio on the crystallization of TS-1 was carried out using the formula of $SiO_2:xTiO_2:0.4NaOH:0.3TPA:114H_2O$ (x = 100.00, 33.33, 20.00, 14.29, 10.00, 7.69, 5.88 and 5.0). The reaction condition was set at 150°C reaction temperature and 110 h aging time while the reaction time was varied from 15 to 35 h depending on the Ti loaded. Figure 4.12 shows the FT-IR spectra of TS-1 samples a-h. The peak at 960 cm^{-1} attributed to a stretching mode of an [SiO$_4$] unit bonded to a Ti^{4+} ion (O$_3$SiOTi) representing the incorporation of titanium in the MFI framework. The ratio of the peak at 960 and 800 cm^{-1} can be related to the titanium content in the zeolite structure. Figure 4.12 shows that the samples synthesized in the presence of titanium have higher 960/R800 ratios as increasing the element content in the solid. The DR-UV spectra of the samples a-h are shown in Figure 4.13. The strong peak at 210 nm was assigned to the tetracoordinated titanium in the zeolite framework. The broad band peak at 280 nm indicated the partially polymerized hexacoordinated Ti species, which contain Ti-O-Ti and were belong to a silicon-rich amorphous phase. The band at 330 nm, which assigned to the extra-framework anatase phase, is shown in sample h. The peaks at both 210 and 280 nm are increased as titanium content increased. The peak at 280 nm increases stronger than that at 210 nm for the sample f due to the hexacoordinated Ti species formation at higher titanium loaded. It can be stated that this synthetic method using microwave irradiation has provided TS-1 catalysts with higher Ti content for lower synthesis time, as compared to the conventional procedures (1-10 days). This is significant when compared to the previous reports on the synthesis of TS-1 under microwave heating where the samples were in the range of Si/Ti molar ratio of 50-70. In our study, the samples prepared have the Si/Ti ratio up to 5.88. The SEM results are shown in the figures 4.14 (a-h). Changing The Si/Ti loading ratio slightly influenced the morphologies of synthesized products.
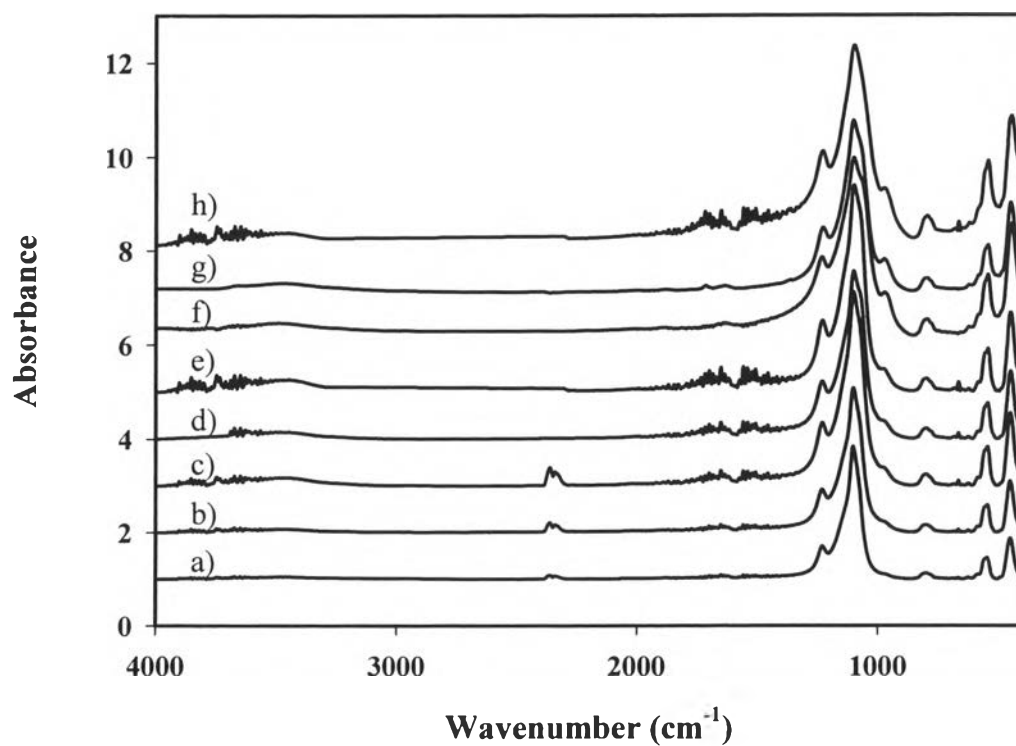
Figure 4.12 FTIR spectra of products formed from the reaction of
SiO$_2$:xTiO$_2$:0.4NaOH:0.3TPA:114H$_2$O with reaction conditions
of 110 hr aging time, 150°C reaction temperature, 15 hr reaction
time for a-b, 20 hr reaction time for c-e, 25 hr reaction time for f
and 35 reaction time for g-h with Si/Ti ratios, x, of: a) 100.0; b)
33.3; c) 20.0; d) 14.3; e) 10.0; f) 7.7; g) 5.9 and h) 5.0.
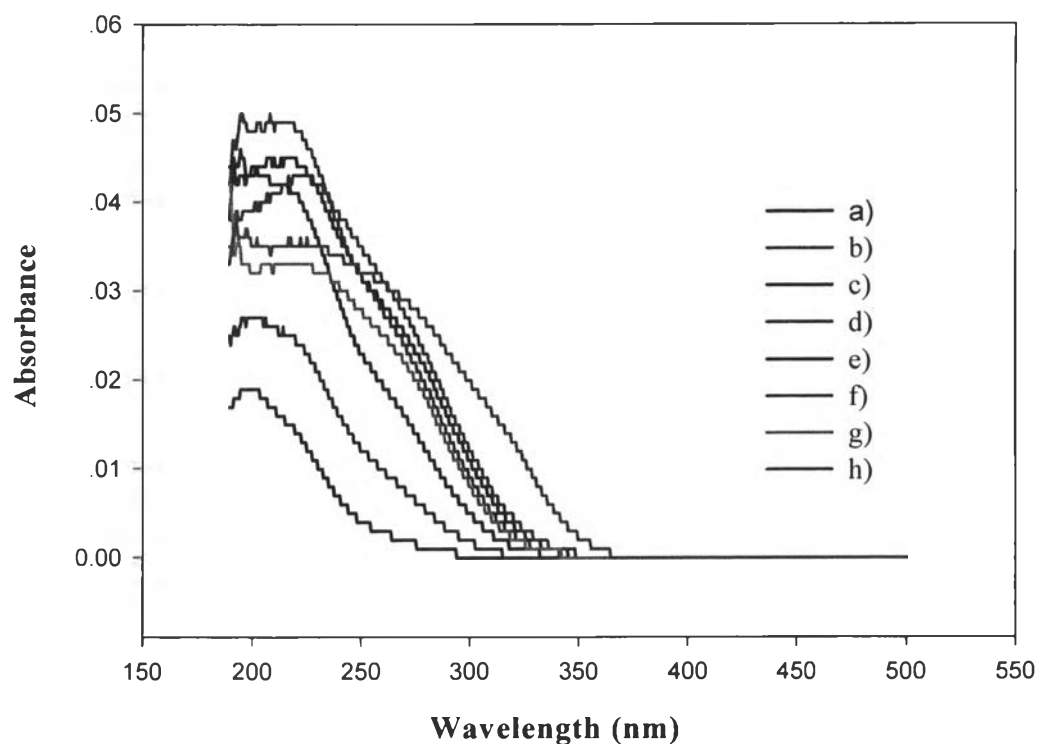
Figure 4.13 DR-UV patterns of products formed from the reaction of
$SiO_2:xTiO_2:0.4NaOH:0.3TPA:114H_2O$ with reaction conditions
of 110 hr aging time, 150°C reaction temperature, 15 hr reaction
time for a-b, 20 hr reaction time for c-e, 25 hr reaction time for f
and 35 reaction time for g-h with Si/Ti ratios, x, of: a) 100.0; b)
33.3; c) 20.0; d) 14.3; e) 10.0; f) 7.7; g) 5.9 and h) 5.0.

Figure 4.14 Effect of the Si/Ti on product morphology formed after aging for
110 hr and heating at 150°C for 15 hr reaction time for a-b, 20 hr
reaction time for c-e, 25 hr reaction time for f and 35 reaction
time for g-h using the Si/Ti ratio, x, of: a) 100.0; b) 33.3;
c) 20.0; d) 14.3; e) 10.0; f) 7.7; g) 5.9 and h) 5.0.